Deodorization and Deacidification of Edible Oils with Dense Carbon Dioxide

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Near-critical carbon dioxide shows potential for extraction of free fatty acids, off-odors or flavors from edible fats and oils. Deacidification and deodorization of a simulated, roasted peanut oil with dense CO_2 was performed at various temperatures, pressures and extraction factors in a pilot-scale, packed extraction column with an i.d. of 2.86 cm and a height of 162 cm. Pyrazine and its derivatives are major components of roasted peanut aroma. At constant temperature and pressure, the distribution coefficient (m) for pyrazine derivatives was inversely related to the degree of substitution of methyl groups (molecular weight) and boiling point, that is, the solubility was directly related to the compounds volatility. CO_2 fluid-phase density alone could not explain the equilibrium solubility behavior of either fatty acids or pyrazines. At constant fluid-phase density, m for pyrazine derivatives decreased with increasing pressure and temperature, while that for fatty acids increased. At 20 MPa pressure, increasing the temperature from 47 to 57°C increased m for pyrazines, but decreased m for fatty acids, indicating that the system was within the retrograde region for fatty acids. Free fatty acid solubility was inversely related to chainlength and, in the supercritical region, directly related to the degree of unsaturation. Deodorization is mass-transfer-controlled, and deacidification is thermodynamically constrained. The efficient deodorization and deacidification of an actual crude oil pressed from roasted peanuts was accomplished by extraction with CO_2 at 47°C and 20 MPa. Extraction with carbon dioxide may be particularly useful for deacidifying expensive specialty fats with high initial acidity, or where the quality and purity of the extracted components are of importance.

KEY WORDS: Deacidification, deodorization, equilibrium solubility, free fatty acids, peanut oil, pyrazines, refining of edible oil.

The purpose of refining edible fats and oils is the removal of nontriacylglycerol components, including free fatty acids, nonhydratable phosphoacylglycerols, sterols, pigments, glucosides, waxes, hydrocarbons and other compounds that may be detrimental to the flavor or oxidative stability of the refined oil (1). Two schemes are generally employed to accomplish this. Chemical refining, or deacidification by neutralization, which is the extraction of the oil with aqueous caustic solution, and physical refining, or deacidification by distillation, which is the steam stripping of the oil at elevated temperature under reduced pressure. Deodorization and heat bleaching of carotenoids are also accomplished by steam stripping. Physical processes are generally preferred over chemical techniques (1).

Alternative processes, such as liquid-liquid extraction with 98% methanol (1) and distillation without the aid of stripping steam (2), have been used to a limited extent to deacidify expensive specialty fats with high initial acidity. The fatty acids obtained from methanol extraction processes are of good quality (1), and alternative refining methods may find application where the quality and purity of the extracted components are of importance.

Many dense gas extraction processes, such as for hops extraction, are semicontinuous, with batch feed of solids. However, there is no conceptual reason why the continuous extraction of a suitable liquid stream with dense gas should not be possible. Zosel (3) described the deodorization of edible oil with carbon dioxide at temperatures of 50–250°C and pressures of 10–25 MPa in a continuous, countercurrent device. Nokolov *et al.* (4) studied the potential application of supercritical carbon dioxide for deacidification of vegetable oil and removal of off-flavor compounds from soybean flour. By comparing solubility isotherms of liquid acids and vegetable oil (triacylglycerols), they concluded that deacidification of oil would be possible. Based on their studies, pressures from 15 to 20 MPa and temperatures at or above 50°C would result in higher selectivity for fatty acids than for triacylglycerols. Brunetti *et al.* (5) have illustrated the feasibility of using supercritical carbon dioxide for deacidification of olive oil, especially at high free fatty acid contents. However, their data were limited to the selectivity of the fatty acids and pure and mixed triglycerides. DeHaan *et al.* (6) have demonstrated the feasibility of extracting flavor from milk fat with carbon dioxide in a packed column.

Deacidification and deodorization of edible oils are two potential applications for extraction with dense carbon dioxide. The design of such a process requires knowledge of equilibrium solubility (thermodynamic constraints), as well as of mass transfer rate (kinetic constraints). Unlike classical extraction with two immiscible liquids, when an edible oil comes in contact with dense carbon dioxide, a large amount of CO_2 dissolves in the oil phase. The weight fraction of carbon dioxide in palm oil during supercritical extraction is typically of the order of 0.39 at 50°C and 20.81 MPa (7). With such high mutual phase solubility, the density, viscosity, surface tension and solute concentration of the liquid phase will change dramatically with temperature and pressure. This, in turn, affects the hydrodynamic behavior and kinetics of mass transfer in a manner that is not fully understood.

The purpose of this work was to obtain equilibrium and mass transfer data to evaluate extraction with dense CO_2 for the deodorization and deacidification of roasted peanut oil.

METHODS

Materials. Pyrazine and its derivatives are major components of roasted peanut odor (aroma) (8). The fatty acid composition of peanut oil comprises 52–78% of oleic (C18:1), linoleic (18:2) and palmitic acid (C16:0) (9). Refined soybean oil (courtesy of Van Den Bergh Foods Co., Baltimore, MD) was used as the carrier feed solvent, and to simulate roasted peanut oil it was fortified with oleic (CAS#112-80-1; Eastman Kodak Co., Rochester, NY) and palmitic (P0625; Sigma Chemical Co., St Louis, MO) acids for modeling deacidification, and with pyrazine (P2145;

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TABLE 1

Free Fatty Acid Composition of Original Refined Soybean Oil

Fatty acid	Weight %
C14:0	0.0053
C16:0	0.0175
C18:0	0.0113
C18:1	0.0230
C18:2	0.0517

Sigma Chemical Co.), 2-methyl pyrazine (ICNFLOW, 151673; ICN Biomedicals, Inc., Costa Mesa, CA) and 2,5-dimethylpyrazine (ICNFLOW, 150949; ICN Biomedicals, Inc.) for modeling deodorization. The total free fatty acid content used for the studies was 1–4% by weight. Concentrations of pyrazine and its derivatives were 0.01–0.1% by weight. The free fatty acid content of the original refined soybean oil is presented in Table 1. For verification of the process, oil pressed from roasted peanuts was obtained from commercial sources.

Flavor compounds used to enrich the soybean oil were all ≥99% in purity. Palmitic acid was only 95% pure, containing approximately 2.8% stearic acid, 1.2% oleic acid and 1% linoleic acid. Oleic acid was only 63.7% pure, containing 10.3, 6.6 and 2.3% of linoleic, palmitic and stearic acid, respectively. Each oil sample was characterized by gas chromatography before and after each extraction. Liquefied CO_2 (≥99 mol%; Union Carbide Co., Danbury, CT) was drawn from cylinders equipped with siphon tubes.

Equipment. An experimental apparatus was designed and constructed to refine edible oil in a packed-column-type contactor with dense carbon dioxide as the solvent. A schematic diagram for the system is presented in Figure 1.

The column was constructed in two sections of 2.86 cm nominal i.d. 316 stainless steal pipe and packed with stainless steel mesh packing (Goodloe®, Glitsch, Inc., Dallas, TX) along a contact height of 162 cm. Four heating bands (#B1L4ER1; Watlow, Co., St. Louis, MO), controlled by microprocessor-based auto-tuning PIC controllers (SR22; Shimaden Co., Ltd., Tokyo, Japan) were used to regulate the column temperature. Temperature control to within ± 1.0°C was possible at flow rates above 15 g/min. However, at low CO_2 flow rates the temperature was observed to vary by ± 5.0°C. View cells (visual extraction vessels; Bioseparations, Inc., Ithaca, NY) were placed at either end of the column to permit observation and control of the fluid interface, *e.g.*, to prevent flooding. The dispersed CO_2 phase distributor was embedded in the packing to prevent premature flooding (10).

High-pressure, controlled-volume, air-driven liquid pumps (Haskel, Inc., Burbank, CA) were used to pump feed (M-71, with single-stroke modification) and solvent (DSF-60, with low-pressure control and single-stroke modification). To prevent cavitation in the solvent pump, CO_2 was precooled in a double-coil heat exchanger (DHTC-SS-4-Z; Parker Hannifin Corp., Huntsville, AL) and a circulating, refrigerated water bath (Haake D8-GH; Fisons Instruments, Valencia, CA). Autopulse® repeat cycle timers (Haskel, Inc.) were used to control solvent and feed flow rates.

CO_2 solvent and oil feed temperatures were controlled with double-coil heat exchangers (DHTC-SS-4-Z) and circulating, refrigerated water baths (Haake F3-CH with external RTD located in the solvent stream; and Masterline 2095, Forma Scientific, Marietta, OH, respectively). The extraction column pressure was controlled with a back pressure regulator (Series 26-1700; Tescom, Elk River, MN), and the liquid raffinate flow was regulated with a micrometering valve (SS-31RS4, Whitey Co., Highland Heights, OH).

Column pressure was monitored by a pressure transducer (PX302-5KGV) and digital process indicator (DP280; Omega Engineering, Inc., Stamford, CT). An electronic mass flow meter (HFM-200 with PR-4A digital readout monitor) and totalizer (TR-1; Teledyne Hastings-Raydist, Hampton, VA) were used to measure fluid-phase, CO_2, flow. Carbon dioxide in the raffinate was measured with a totalizer (DTM-115; American Meter Div., Singer). The liquid raffinate mass flow rate was measured manually.

Extraction methodology. The column was operated with the liquid oil as the continuous phase entering at the top of the column, and the carbon dioxide solvent as the dispersed phase bubbling up from the bottom.

The distribution coefficient of a solute, i, m_{is}, is a measure of the relative dispersed-phase (y phase) and continuous-phase (x phase) capacities for the solute at equilibrium, and is defined as:

$$m_{is} = y^*_{is}/x^*_{is} \quad [1]$$

where y* and x* denote mass fraction of solute at equilibrium. A procedure adapted from Lahiere (11) was used to measure the distribution coefficients. Equilibrium was determined by operating at "pinched" conditions at the top of the column. This was done by holding the liquid flow rate constant and decreasing the solvent flow to a point beyond which the concentration of solute in the extract at steady state did not increase. Because of the dilute concentration of solute in the liquid phase, the equilibrium line was assumed to be linear.

Solubility of a nonvolatile solute in a supercritical fluid has been correlated to solvent density (12). Because the intention was to study mass transfer rates under differing hydrodynamic conditions, *e.g.*, fluid-phase viscosity, keeping equilibrium solubility constant, three systems were chosen with equivalent solvent densities. A fourth system, with both lower fluid density and viscosity, was also chosen (Table 2).

The experimental protocol was as follows: (i) prior to beginning a run, all water baths were brought to their operating temperatures; (ii) the column was filled to 2/3 its volume with oil and pressurized to approximately 6 MPa (900 psi) by opening the CO_2 cylinder; (iii) the heating bands were activated, and the operating pressure was attained by starting the solvent pump and adjusting the back pressure regulator; (iv) the system was run for 5 min to stabilize the CO_2 flow rate before starting the liquid pump; (v) the liquid pump was started, and the micrometering valve was opened and adjusted until the CO_2 mass flow meter returned to its original reading.

The CO_2 in the raffinate was measured by closing the valve at the bottom of the raffinate collector and opening the valve at the top. Collection of raffinate samples

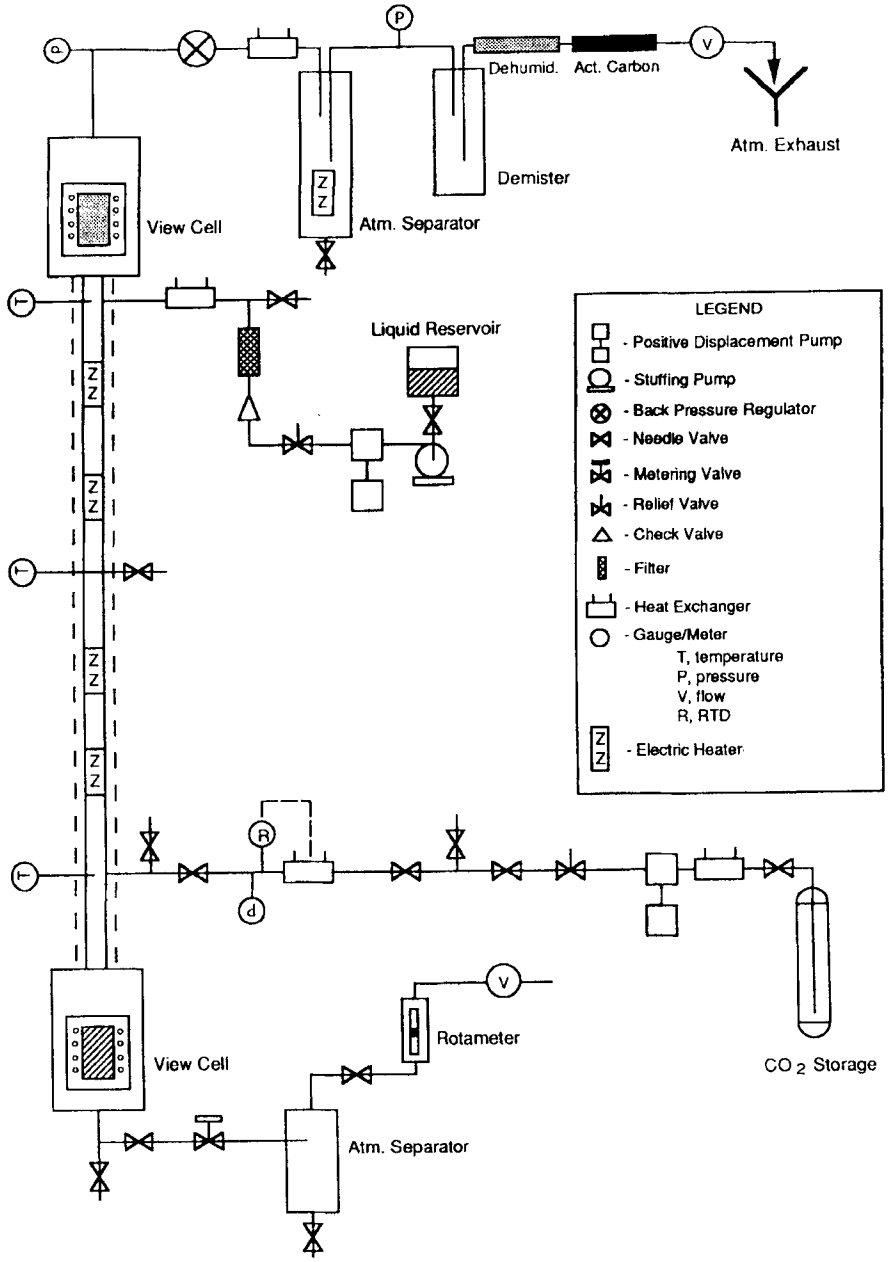

FIG. 1. Schematic diagram of the extraction system. Dehumid, dehumidifier; Atm., atmosphere.

TABLE 2

Experimental Conditions

System	Temperature (°C)	Pressure (MPa)	Density (g/cm^3)[a]	Viscosity (cp)[b]	Solubility of CO_2 in oil (g/g)[c]	State
A	27	10.1	0.803	0.0665	0.23	Liquid
B	37	15	0.803	0.0703	0.31	Supercritical
C	47	20	0.803	0.0714	0.38	Supercritical
D	57	20	0.744	0.0626	0.23	Supercritical

[a]Density of CO_2. Reference 13.
[b]Viscosity of CO_2. Reference 14.
[c]Determined experimentally.

for further analysis was begun after one liquid elution cycle time (column void volume/liquid volumetric flow). Extract was collected from a temperature-controlled separator located downstream of the back-pressure regulator. Expanded CO_2 gas from the separator passed through a demisting chamber, a dewatering column and an activated charcoal column before entering the mass flow meter.

Sample analysis. A quantitative method of analysis for the basic fraction of flavor compounds (pyrazine and its derivatives) of peanut oil was derived from the specific group analysis method (15): (i) peanut oil was dissolved into ethyl ether and hydrochloric acid solution (pH = 1) to make the basic fraction compounds water-soluble; (ii) the aqueous solution was washed with pentane/ether (2:1) to remove any nonbasic organic compounds; (iii) the pH of the aqueous solution was increased with sodium hydroxide solution (pH = 9); (iv) the basic compounds were extracted with pentane/ether (2:1); (v) this extract was dried with sodium sulfate; and (vi) the volume was reduced under nitrogen gas. Pyridine was added as an internal standard for quantitation of flavor compounds. Due to differences in pKa and volatility, the relative recovery of pyrazine and its derivatives was not constant, and calibration was required for each sample preparation. To do so, a control sample with a known amount of pyrazine, 2-methylpyrazine, 2,5-dimethylpyrazine and pyridine was run along with each sample.

To separate fatty acids from the oil samples prior to quantitation, samples were dissolved in hexane and applied to a hexane-prewashed aminopropyl-bonded solid-phase extraction column (Superclean™ LC-NH_2 #57014; Supelco, Inc., Bellefonte, PA). Lipid classes were eluted with chloroform/2-propanol (2:1), 2% acetic acid in diethyl ether (free fatty acids) and 2% acetic acid in methanol (16). Pentadecanoic acid (C15:0) was added as an internal standard. After elution and evaporation of the solvent under nitrogen gas, free fatty acids were recovered and methylated with BF_3-methanol for gas chromatographic analysis (17).

Approximately 1 μL of sample (pyrazines or fatty acid methyl esters) was injected onto a Supelcowax™-10 fused-silica capillary column (30 m length, 0.53 mm i.d. and 0.5 μm film thickness; Supelco, Inc.). The column was installed in a gas chromatograph (5890A; Hewlett-Packard Co., Avondale, PA) with an on-column injection port, flame-ionization detector and integrator (3396A; Hewlett-Packard). Helium was used as the carrier gas. For fatty acid analysis, the column was run isothermally at 200°C with a detector temperature of 220°C. For pyrazine analysis, the temperature was programmed from 80°C (10-min hold) to 160°C (20-min hold) at a rate of 2°C/min, with a detector temperature of 200°C.

RESULTS AND DISCUSSION

Preliminary experiments included material balances around the column (Table 3). The overall mass balance and component balances for fatty acids were good; measured concentrations differed by only 2–6% from those expected. However, the amount of pyrazines recovered in the extract was much less than that expected. It appears that pyrazines were stripped out of the separator by carbon dioxide gas because the amount recovered was inversely related to the volatility of the compound. For determination of distribution coefficients, the concentration of solute in the extract was calculated from material balances by using experimentally determined values of solute concentrations in the feed, x_{in}, and raffinate, x_{out}, and assuming that the concentration of solute entering with the solvent, y_{in}, was zero.

Figure 2 illustrates the effect of solvent-to-feed ratio (G/L) on the distribution coefficients of free fatty acids and pyrazines. The distribution coefficients for free fatty acids appeared to reach constant values at solvent-to-feed ratios of ≤4. However, m for pyrazines continued to increase at G/L < 1. At constant temperature and pressure, m for pyrazine derivatives was inversely related to the degree of substitution of methyl groups (molecular weight) and boiling point (115, 136 and 155°C for pyrazine, 2-methylpyrazine and 2,5-dimethylpyrazine, respectively), *i.e.*, m was directly related to the compounds volatility (Table 4). Despite having the lowest solvent density, the highest value of m for pyrazine and 2-methylpyrazine was obtained with system D. An increase in temperature from 47 to 57°C, comparing system C with D, increased m for the pyrazines. At constant fluid-phase density, m for pyrazine derivatives decreased with increasing temperature and pressure. The solubility of free fatty acids decreased with an increase in carbon chainlength (molecular weight). In the supercritical region (systems B–D), fatty acid solubility increased with the degree of unsaturation. At constant fluid-phase density, distribution coefficients for fatty acids increased with temperature and pressure (Table 4). At 20 MPa pressure, increasing the temperature from 47 to 57°C decreased m, indicating that the system was in the retrograde region for fatty acids. Distribution coefficients for liquid-liquid extraction of free

TABLE 3

Component Mass Balances[a]

Compound	x_{in} (wt%)	x_{out} (wt%)	y_{out} (wt%) (measured)	y_{out} (wt%) (calculated)	% Difference
Pyrazine	0.0378	0.0055	0.0003	0.0015	−80
2-Methylpyrazine	0.0463	0.0062	0.0009	0.0019	−53
2,5-Dimethylpyrazine	0.0485	0.0078	0.0013	0.0019	−32
C16:0	1.0618	0.3906	0.0316	0.0311	+2
C18:1	1.0188	0.4453	0.0249	0.0266	−6
C18:2	0.1610	0.0895	0.0031	0.0033	−6

[a]Liquid (oil) phase mass flow rate (L) = 4.3 g/min, gas (CO_2) phase mass flow rate (G) = 92.8 g/min, temperature (T) = 27°C, pressure (P) = 10.1 MPa.

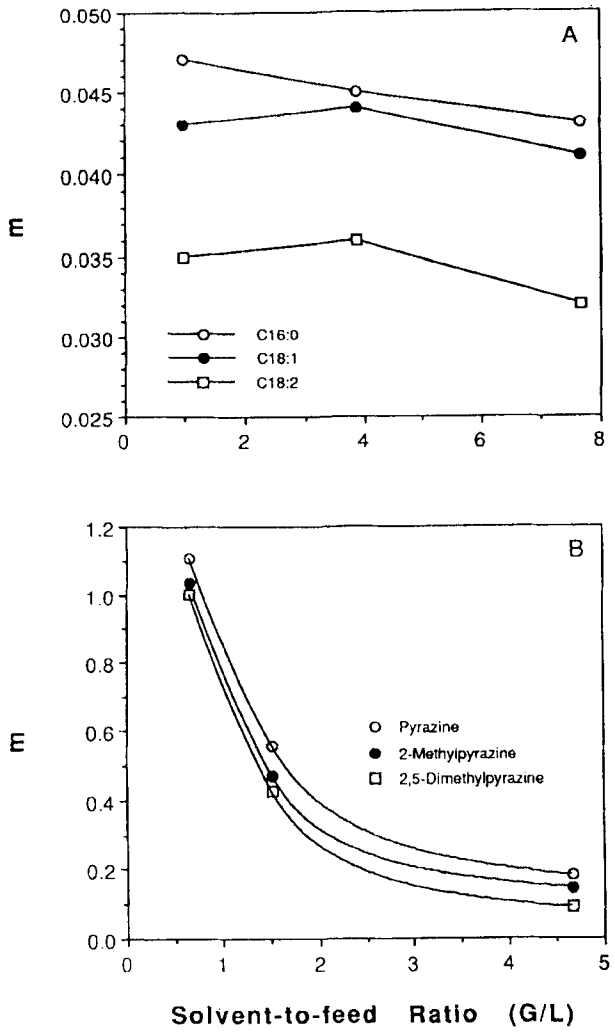

FIG. 2. Distribution coefficients of free fatty acids (A) and pyrazines (B) as a function of solvent-to-feed ratio (L = 21–24 g/min, P = 10.1 MPa, T = 27°C). Abbreviations: L, liquid (oil) phase mass flow rate; P, pressure; T, temperature.

fatty acids from oils with methanol are on the order of 0.024 (1), less favorable than extraction with CO_2.

Dissolution of CO_2 may reduce oil viscosity by an order of magnitude (7,18), enhancing mass transfer rates. A decrease in interfacial tension, resulting from CO_2 dissolution, would also enhance mass transfer, whereas dilution of the solute concentration in the liquid phase would tend to reduce it. The solubility of CO_2 in soybean oil is reported in Table 2. Extraction efficiencies, *i.e.*, the fraction of solute remaining in the raffinate (x_{out}/x_{in}), are reported in Table 5. Despite the fact that system C was least favorable thermodynamically (m was lowest), deodorization efficiency was the highest (x_{out}/x_{in} was the lowest). Similarly, system A showed the lowest deodorization efficiency despite its high m value. This suggests that the extraction of pyrazines was mass-transfer-controlled. This is consistent with Figure 2B. Mass transfer may be enhanced in systems B–D because the CO_2 is in the supercritical state. For system C in particular, mass transfer resistance in the liquid phase would be reduced by the large amount of dissolved CO_2. System C is favorable, both thermodynamically and kinetically, for deacidification. Therefore, it is not surprising that the extraction of free fatty acids is most complete for this set of conditions. However, the extraction efficiency is a strong function of distribution coefficient (Fig. 3), suggesting that deacidification is largely thermodynamically constrained. This is also consistent with Figure 2A.

System C was selected for refining of a crude oil pressed from roasted peanuts because it was favorable for both deodorization and deacidification purposes. CO_2-refined peanut oil was virtually free of any detectable basic aroma compounds after extraction (Fig. 4), while at the same time, 85.2, 80.2 and 84.4% of C16:0, C18:1 and C18:2, respectively, were removed (Fig. 5).

The objectives of classical physical refining are: (i) the removal of odoriferous volatile compounds; (ii) the removal of residual amounts of free fatty acids; (iii) the heat blanching of carotenoids; and (iv) the rendering of the oil, by means of some chemical change, as more flavor-stable during its shelf life (1). This is accomplished by steam-stripping at elevated temperatures (180–240°C) and under vacuum (3–6 mm Hg) (19). The corrosive nature of fatty acids at high temperature, which mandates stainless steel construction, and special high-pressure water boilers required to achieve operating temperature, increase the capital costs of physical refining processes. Working under reduced pressure, equipment for physical refining is subject to safety controls similar to autoclaves (1).

Like conventional physical refining, deodorization and deacidification with dense CO_2 has environmental benefits *vis-a-vis* alkali refining. Additional benefits may also be realized. Large volumes of stripping steam mandate

TABLE 4

Distribution Coefficients as Influenced by Temperature and Pressure[a]

Compound	m (27/0.1)	m (37/15)	m (47/20)	m (57/20)
Pyrazine	1.109	1.046	0.917	1.187
2-Methylpyrazine	1.036	0.930	0.879	1.092
2,5-Dimethylpyrazine	1.001	0.746	0.734	0.834
C16:0	0.047	0.068	0.158	0.132
C18:1	0.043	0.057	0.102	0.092
C18:2	0.035	0.070	0.105	0.101

[a]L = 21–24 g/min, G/L = 0.6–0.7 for pyrazines, 1.0–1.45 for free fatty acids. See Table 3 for abbreviations.

TABLE 5

Extraction Efficiencies for Pyrazine Derivatives and Free Fatty Acids from Soybean Oil[a]

Compound	x_{out}/x_{in} (27/10.1)[b]	x_{out}/x_{in} (37/15)	x_{out}/x_{in} (47/20)	x_{out}/x_{in} (57/20)
Pyrazine	0.132	0.120	0.118	0.120
2-Methylpyrazine	0.122	0.120	0.112	0.120
2,5-Dimethylpyrazine	0.131	0.124	0.107	0.118
C16:0	0.400	0.328	0.183	0.210
C18:1	0.420	0.367	0.243	0.265
C18:2	0.470	0.323	0.238	0.249

[a]L = 6–8 g/min, G/L = 30–32. See Table 3 for abbreviations.
[b]Numbers in parentheses are temperature/pressure.

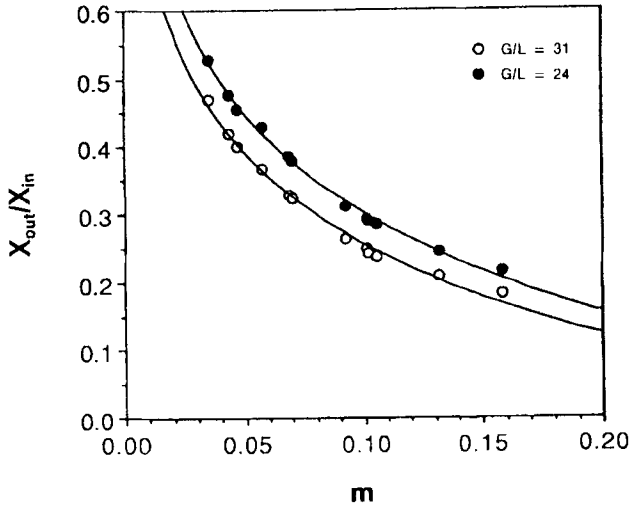

FIG. 3. Extraction efficiency as a function of distribution coefficient for free fatty acids. G/L, solvent-to-feed ratio. Abbreviations: G, gas (CO_2) phase mass flow rate in g/min; see Figure 2 for other abbreviation.

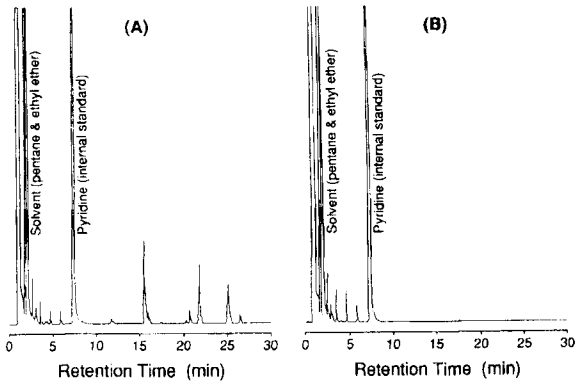

FIG. 4. Gas chromatographic profile of basic flavor compounds in peanut oil before (A) and after (B) CO_2 refining (47°C, 20 MPa, L = 6.2 g/min, G = 178.7 g/min). For abbreviations see Figures 2 and 3.

sizable distillation units and result in oil loss through entrainment. Lower volumetric flow rates for dense CO_2 may result in considerably smaller contactors for the same oil throughput. The use of lower temperatures with CO_2 extraction suggests potential energy savings. However, it is questionable whether CO_2 refining can accomplish steps (iii) and (iv) listed above. Further analysis of refining with dense CO_2 is warranted.

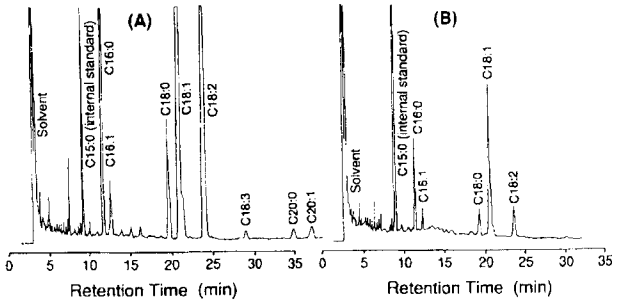

FIG. 5. Gas chromatographic profile of free fatty acids in peanut oil before (A) and after (B) CO_2 refining (47°C, 20 MPa, L = 6.2 g/min, G = 178.7 g/min). See Figures 2 and 3 for abbreviations.

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[Received February 19, 1993; accepted August 4, 1993]